

**REMARKS**

Favorable reconsideration and allowance of the claims of the present application are respectfully requested.

Applicants have amended claims 1, 2, 4, 6, 7, 9, 10, 12, 14, 17, 19-21, 26, 30, 31, 34-36, 38-40, 45, 48, 49, and 55, and cancelled claims 37, 41-44, 46, 47, 51-54, 58, and 59 without prejudice. Claims 78 and 79 were previously cancelled without prejudice. Furthermore, in response to the finality of the restriction requirement, claims 62-69, 72-77, 80, and 81 have been withdrawn. Accordingly, claims 1-36, 40, 45, 48-50, 55-57, 60, 61, 70, and 71 are currently under consideration.

Claim 1 has been amended in several ways, as follows. Most significantly, the crystallization step (e) of claim 1 has been amended by further specifying the arabinose content (purity) as more than 65% on DS (support is found, for example, at page 27, last paragraph of the application as filed); further specifying a galactose content of less than 5% on DS (support is found, for example, at page 25, lines 1-4 of the application as filed, as well as claim 47 as originally filed); further specifying that crystallization is accomplished by boiling, seeding with seed crystals of arabinose, and continued boiling after seeding, to obtain a crystal yield of 1 to 60% on arabinose and a dry solids content of the crystal mass of over 60%, followed by cooling (support is found, for example, at page 25, last paragraph, and Example 15B of the application as filed); and further specifying that the obtained crystalline arabinose has an arabinose content of more than 98% on DS (support is found, for example, at page 28, next to the last paragraph of the application as filed, as well as claim 54 as originally filed). Claim 1 has also been amended by replacing the phrase "rich in" with the term "containing";

removing the term "controlled" from step (a); incorporating the active tense (e.g., "hydrolyzing" in place of "hydrolysis"); and defining the expression "DS" as "dry substance content" in its first occurrence (see page 11, lines 11 and 12 from bottom of the application as filed). Similar amendments have been made to other claims.

Different clarifying amendments have been made to other claims. For example, Applicants have clarified claims 35, 38, and 39 by replacing the phrase "said hydrolyzate" with "said clarified hydrolyzate", as recited in claim 1.

No new matter has been added to the application.

The Office Action objects to claims 34-38 and 70 for allegedly failing to further limit the subject matter of the claim they depend from. As grounds for the rejection, the Office Action contends that the indicated claims fail to recite additional steps related to the recovery of arabinose (the purpose of the claimed method as stated in the preamble of claim 1). The Office Action cites 37 C.F.R. §1.75(c) for alleged support of these grounds.

Nevertheless, Applicants disagree that the indicated claims are unrelated to the recited purpose of the independent claim (i.e., recovery of arabinose and optionally at least one other monosaccharide.) Contrary to the allegations of the Office Action, the objective is to purify the vegetable fiber to recover arabinose, and optionally at least one other monosaccharide. In particular, the rejected claims are directed to the processing of secondary fractions (i.e., optionally at least one other monosaccharide) produced during the claimed process for recovering arabinose. These secondary fractions are recited in claim 1. Thus, the indicated dependent claims further limit the subject matter of claim 1.

Moreover, Applicants respectfully assert that the patent regulation provided under 37 C.F.R. §1.75(c) does not in any way stipulate that a dependent claim is improper for delineating process steps on byproduct or other compositions produced in the course of producing a primary recited composition of the independent claim. Instead, 37 C.F.R. §1.75(c) requires, simply, that a dependent claim must further limit the scope of a claim from which it depends. The indicated dependent claims adhere to 37 C.F.R. §1.75(c) by describing methods for processing the secondary fractions i.e., towards producing at least one other monosaccharide recited in claim 1. The indicated dependent claims, thus, further limit the scope of the claim from which they depend.

Accordingly, Applicants consider claims 34-38 and 70 to be proper dependent claims. Applicants, thus, respectfully request that the foregoing claim objections under 37 C.F.R. §1.75 be withdrawn.

The Office Action also objects to claim 1 for use of hyphens in certain words. The Office Action also objects to claim 29 for reciting a zero ("0") instead of an "O". The Office Action also objects to claim 1 for reciting the abbreviation "DS" without providing a definition, at least in its first occurrence. Applicants have amended the claims in compliance with the foregoing objections. Accordingly, the indicated claims should no longer be subject to these objections.

The Office Action rejects claims 1-61, 70, and 71 under 35 U.S.C. §112, second paragraph for alleged indefiniteness. In particular, the Office Action alleges that there is insufficient antecedent basis in claim 1 for the limitations "said aqueous hydrolyzate" in line 10, as well as "undissolved solids" in line 12. However, Applicants assert that proper antecedent basis has been established by prior recitation of these terms

in lines 6 and 9, respectively, of claim 1. Accordingly, Applicants respectfully request that the foregoing 35 U.S.C. §112, second paragraph rejections be withdrawn.

The Office Action also considers the following terms to be indefinite: "rich" in claims 1, 2, 4, 6, 7, and 9; "strongly" in claims 22, 23, 28, and 29; "controlled" in claim 1; and "weakly" in claims 24, 25, and 27. Responsive thereto, Applicants have replaced the term "rich in", as found in the indicated claims, with the term "containing". Applicants have also removed the term "controlled" from claim 1. Regarding the terms "strongly" and "weakly", these terms, when recited as part of the phrase "strongly acid cation exchange resins" (claims 22 and 23), "strongly basic anion exchange resins" (claims 28 and 29), "weakly acid cation exchange resins" (claims 24 and 25), or "weakly basic anion exchange resins" (claim 27), have a clear and well-understood meaning to one skilled in the art of chemistry and chemical separation methods. As support, Applicants direct the Examiner to the reference Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GMBH & Co., "Ion Exchangers", © 2008 (in particular, pages 4 and 5 therein accompanying this Response). Accordingly, Applicants respectfully request that the foregoing 35 U.S.C. §112, second paragraph rejections be withdrawn.

The Office Action also considers claim 1 to be indefinite for allegedly requiring in step (c) the process steps described in step (b), even though step (b) is recited as an optional step. However, Applicants consider the grounds of this rejection to be factually incorrect since step (c) recites the following: "separation of undissolved from said aqueous hydrolyzate obtained in step (a) or when step (b) is performed, from said neutralized hydrolyzate obtained in step (b) to obtain a clarified hydrolyzate..." (emphasis

added) Applicants thus maintain that claim 1 is definite. Applicants, therefore, respectfully request the foregoing 35 U.S.C. §112, second paragraph rejection to be withdrawn.

The Office Action also rejects claims 1, 10, 12 as allegedly indefinite for use of the term "controlled". The Office Action also rejects claim 49 as allegedly indefinite for use of the term "single-stage". However, as these terms have been removed in the instant claim amendments, the foregoing indefiniteness rejections are now moot.

Claims 1-5, 9-18, 33, 39, 41, 44-48, 51-61, and 71 stand rejected under 35 U.S.C. §102(b) as allegedly anticipated by Ingle et al. (*Research and Industry*, vol. 30, pp. 369-373, Dec. 1985). Separately, claims 1-3, 6, 9-18, 20-29, 32, 33, 40, 44-48, 51-54, 60, 61, and 71 stand rejected under 35 U.S.C. §102(b) as allegedly anticipated by U.S. Patent 6,506,897 to Antila et al.

However, the subject matter of claim 42 has been incorporated into claim 1 (the sole independent claim). The subject matter of claim 42 incorporated into claim 1 further specifies the crystallization step (e) as including boiling crystallization combined with cooling crystallization. Step (e) of claim 1 has been further specified beyond the recitation of claim 42 by reciting therein that crystallization is accomplished by boiling, seeding with seed crystals of arabinose, and continued boiling after seeding, to obtain a crystal yield of 1 to 60% on arabinose and a dry solids content of the crystal mass of over 60%, followed by cooling to obtain high purity crystals of arabinose. Inasmuch as Claim 42 is not subject to the foregoing §102(b) rejections, Applicants assert that the claims, as amended, are no longer subject to the foregoing §102(b) rejections. Thus, this rejection is obviated; withdrawal thereof is respectfully requested.

Claims 1-5, 9-19, 30, 31, 33, 39, 44-48, 51-61, and 71 stand rejected under 35 U.S.C. §103(a) as allegedly obvious in view of Ingle et al. combined with U.S. Application Pub. No. 2002/0153317 to Heikkila et al. Separately, claims 1-3, 6, 9-19, 20-33, 40, 44-48, 51-54, 60, 61, and 71 stand rejected under 35 U.S.C. §103(a) as allegedly obvious in view of Antila et al. combined with U.S. Application Pub. No. 2002/0153317 to Heikkila et al. However, as the subject matter of claim 42 has been incorporated into claim 1 (the sole independent claim), and claim 42 is not subject to the foregoing §103(a) rejections, Applicants assert that the claims, as amended, are no longer subject to the foregoing §103(a) rejections.

Claims 1-5, 9-18, 30, 39, 41-48, 50-61, and 71 stand rejected under 35 U.S.C. §103(a) as allegedly obvious in view of Ingle et al. combined with U.S. Application Pub. No. 2001/0018544 to Burdet et al. and U.S. Patent 4,835,152 to Korosi et al. In making the rejection, the Office Action acknowledges that Ingle et al. does not teach the feature of claim 42 (now incorporated into claim 1) that crystals are obtained by boiling, cooling, and washing the crystals. In this regard, the Office Action contends that these deficiencies are compensated, first by Korosi et al., by the alleged teaching therein of obtaining purified crystalline benzodiazepine derivatives by boiling the crude crystals, cooling the solution, and washing the resulting crystals (Office Action cites col. 6, lines 61-64 of Korosi et al. for alleged support). The Office Action further contends that the deficiencies found in Ingle et al. are further compensated by the alleged teaching in Burdet et al. of obtaining crystals of a carotenoid derivative by boiling the carotenoid derivative in a reaction mixture, cooling to room temperature to obtain crystals, filtering,

and then washing to yield the desired crystals (Office Action cites par. 0195 of Burdet et al. for alleged support).

However, claim 1, as amended, does not simply recite boiling and cooling to obtain crystals, as taught in Korosi et al. and Burdet et al. In particular, claim 1, as amended, further specifies that crystallization is achieved by seeding the boiling solution containing arabinose, and continuing to boil the solution after seeding. Korosi et al. and Burdet et al. do not teach or in any way suggest at least the foregoing features of claim 1 that crystals are obtained by seeding a boiling solution, and continuing to boil the solution after seeding. As discussed in page 25, last paragraph of the application as filed, the particular boiling-seeding-cooling method of crystallization, as claimed, is advantageous over simple boiling and cooling for the reason that an improved crystal size distribution and yield of arabinose is achieved. Although compounds that are structurally unrelated to arabinose (such as those disclosed in Korosi et al. and Burdet et al.) are commonly and effectively crystallized by simple boiling and cooling methods, these simple methods are not capable of providing arabinose crystals in the purity and yield provided by the crystallization methodology delineated in step (e) of claim 1, as amended.

Furthermore, in contrast to the aqueous solutions employed in crystallization of arabinose in accordance with the claimed invention, Korosi et al. and Burdet et al. teach completely non-aqueous solutions for achieving their crystallizations. For example, in the portion of Korosi et al. relied upon by the Office Action (i.e., col. 6, lines 61-64), Korosi et al. teaches suspending the crude product in isopropanol to achieve crystallization; and in the portion of Burdet et al. relied upon by the Office Action (i.e.,

par. 0195), Burdet et al. teaches dissolving the compound to be crystallized in methylene chloride, followed by the addition of ethanol. Thus, the combination does not teach, disclose or suggest those of aqueous solution to effect crystallization of arabinose as claimed.

Accordingly, Applicants have shown that the claims, as amended, are non-obvious, and hence, patentable in view of the combination of Ingle et al., Korosi et al., and Burdet et al. Applicants, thus, respectfully request that the 35 U.S.C. §103(a) rejection citing these references be withdrawn.

Claims 1-3, 6, 9-19, 20-29, 32, 33, 40-48, 50-54, 60, 61, and 71 stand rejected under 35 U.S.C. §103(a) as allegedly obvious in view of Antila et al. in combination Burdet et al. and Korosi et al. In making the rejection, the Office Action acknowledges that Antila et al. does not teach the feature of claim 42 (now incorporated into claim 1) that crystals are obtained by boiling, cooling, and washing the crystals. In this regard, the Office Action contends that these deficiencies are compensated by Burdet et al. and Korosi et al., for the same reasons given above in the preceding §103(a) rejection.

However, in response to the above §103(a) rejection, Applicants herein incorporate the arguments presented above that demonstrate the substantial deficiencies in Burdet et al. and Korosi et al. in teaching or suggesting the claimed crystallization methodology of step (e). Accordingly, Applicants have demonstrated that the indicated claims are non-obvious, and hence, patentable, over Antila et al. in combination with Burdet et al. and Korosi et al. Applicants, thus, respectfully request that the foregoing 35 U.S.C. §103(a) rejection citing these references be withdrawn.

Claims 1-5, 7, 9-18, 33, 39, 41, 44-48, 51-61, and 71 stand rejected under 35 U.S.C. §103(a) as allegedly obvious in view of Ingle et al. combined with Park et al. (*Biotechnology Letters*, 23: 411-416, 2001). However, as the subject matter of claim 42 has been incorporated into claim 1 (the sole independent claim), and claim 42 is not subject to the foregoing §103(a) rejections, Applicants assert that the claims, as amended, are no longer subject to the foregoing §103(a) rejection.

Claims 1-3, 6, 7, 9-29, 32, 33, 40-48, 50-54, 60, 61, and 71 stand rejected under 35 U.S.C. §103(a) as allegedly obvious in view of Antila et al. combined with Park et al. In making the rejection, the Office Action contends that Antila et al. teaches or suggests all of the features of the indicated claims, except the features that the hydrolysis step is achieved by enzymes (as in claim 1), or that the source of the arabinose is corn fibers (as in claim 7). In regard to these deficiencies, the Office Action contends that Park et al. teaches these features.

The Office Action acknowledges that Antila et al. does not teach any crystallization step. However, regardless of what Park et al. may teach regarding the hydrolysis step, Applicants assert that Park et al. does not teach at least the feature of claim 1, as amended, that crystallization is achieved by boiling, seeding with seed crystals of arabinose, continued boiling after seeding, and then cooling, to obtain purified crystals of arabinose. On the contrary, Park et al. does not even teach boiling crystallization or a seeding step (see page 413, left column, last paragraph of Park et al.) More specifically, in the cited portion of Park et al., one is taught a crystallization process in which L-arabinose is crystallized from water at room temperature.

As the Office Action acknowledges that the primary reference, Antila et al., does not teach any such crystallization process, then clearly, the combination of Antila et al. and Park et al. can not teach the claimed crystallization process. Accordingly, since the combination of Antila et al. and Park et al. fails to teach at least one required feature of the instant claims, then the indicated claims are non-obvious over the combination of references. Applicants, thus, respectfully request that the foregoing 35 U.S.C. §103(a) rejection citing these references be withdrawn.

For all the reasons provided, Applicants consider the claims, as amended, to be patentable. Accordingly, allowance of the pending claims is earnestly requested.

Respectfully submitted,



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# Ullmann's Encyclopedia of Industrial Chemistry

## Ion Exchangers

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### Abbreviations and Acronyms:

BV	bed volume
DG	atmospheric degasser
DM	dry matter
DVB	divinylbenzene
EMA	equivalent mineral acidity
eq	equivalents
FMA	free mineral acidity
FR	flow rate
IN	inert resin
MHC	moisture-holding capacity
R	resin
SAC	strongly acidic cation exchanger
SBA	strongly basic anion exchanger
SBC	strongly basic capacity
TAalk	total alkalinity
TDS	total dissolved solids
TH	total hardness
TOC	total organic carbon
U.C.	uniformity coefficient
WAC	weakly acidic cation exchanger
WBA	weakly basic anion exchanger

### Symbols:

$C_p$	weight capacity, eq/L
$C_v$	volume capacity, eq/L
$D$	diffusion coefficient, mol/cm <sup>3</sup>
$J$	ion flux, mol s <sup>-1</sup> cm <sup>-2</sup>
$k$	mass-transfer coefficient, cm/s
$K$	equilibrium constant
$K_A^B$	selectivity coefficient between components A and B
$N$	fouling factor
$P$	weight of resin
$Q$	flow rate, m <sup>3</sup> /h
$r$	radius of ion-exchange bead
$S$	salinity, meq/L
$t$	operating time, h
$V$	volume of resin, m <sup>3</sup>

$X$  mole fraction

$\alpha_A^B$  separation factor between components A and B

$\gamma$  activity coefficient

$\delta$  thickness of Nernst film

## 1. Introduction

**Definition and Principles.** In ion exchange, ions of a given charge (either cations or anions) in a solution are adsorbed on a solid material (the ion exchanger) and are replaced by equivalent quantities of other ions of the same charge released by the solid.

The ion exchanger may be a salt, acid, or base in solid form that is insoluble in water but hydrated. Exchange reactions take place in the water retained by the ion exchanger; this is generally termed *swelling water* or *gel water*. The water content of the apparently dry material may constitute more than 50 % of its total mass.

Figure 1 shows the partial structure of a cation exchanger; each positive or negative ion is surrounded by water molecules.

Ion exchange forms the basis of a large number of chemical processes which can be divided into three main categories: substitution, separation, and removal of ions.

### 1) Substitution.

A valuable ion (e.g., copper) can be recovered from solution and replaced by a worthless one. Similarly, a toxic ion (e.g., cyanide) can be removed from solution and replaced by a nontoxic ion.

### 2) Separation.

A solution containing a number of different ions passes through a column containing

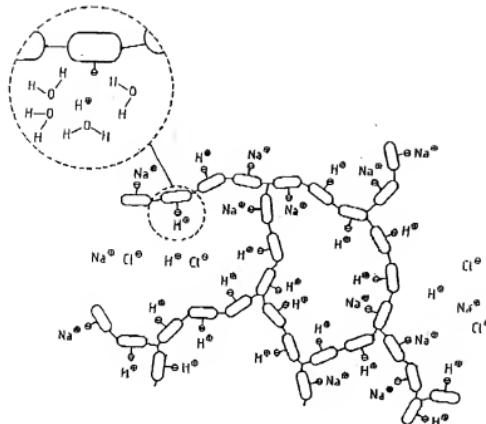


Figure 1. Structure of a cation exchanger that exchanges  $H^+$  for  $Na^+$  ions. Swelling water is represented in the inset.

beads of an ion-exchange resin. The ions are separated and emerge in order of their increasing affinity for the resin.

### 3) Removal.

By using a combination of a cation resin (in the  $H^+$  form) and an anion resin (in the  $OH^-$  form), all ions are removed and replaced by water ( $H^+OH^-$ ). The solution is thus demineralized.

**Historical Aspects.** The discovery of ion exchange dates from the middle of the nineteenth century when THOMSON [1] and WAY [2] noticed that ammonium sulfate was transformed into calcium sulfate after percolation through a tube filled with soil.

In 1905, GANZ [3] softened water for the first time by passing it through a column of sodium aluminosilicate that could be regenerated with sodium chloride solution. In 1935, LIEBKNECHT [4] and SMIT [5] discovered that certain types of coal could be sulfonated to give a chemically and mechanically stable cation exchanger. In addition, ADAMS and HOLMES [6] produced the first synthetic cation and anion exchangers by polycondensation of phenol with formaldehyde and a polyamine, respectively. Demineralization then

became possible. At present, aluminosilicates and phenol-formaldehyde resins are reserved for special applications and sulfonated coal has been replaced by sulfonated polystyrene.

**Polystyrene Resins.** The first polystyrene-based resin was invented by D'ALELIO in 1944 [7]. Two years later, McBURNEY produced polystyrene anion-exchange resins by chloromethylation and amination of the matrix [8].

The anion exchangers known until then were weakly basic and took up only strong mineral acids. The new resins produced by the McBurney process were stronger bases and could adsorb weak acids such as carbon dioxide or silica, allowing complete demineralization of water with a purity previously obtainable only by multiple distillation in platinum. Even today, ion exchange is still the only process capable of producing the water quality needed for high-pressure boilers. Reverse osmosis and electrodialysis can demineralize solutions with 50–90% efficiency. Only ion exchange can "polish" the predemineralized solution with a demineralization efficiency of 99–99.99%.

**Macroporous Resins.** Two of the problems encountered in the use of ion-exchange resins are the fouling of the resin by natural organic

acids present in surface waters and the mechanical stress imposed by plants operating at high flow rates. To cope with these, three manufacturers [9–11] invented resins with a high degree of cross-linking but containing artificial open pores in the form of channels with diameters up to 150 nm that can adsorb large molecules. Resins in which the polymer is artificially expanded by the addition of a nonpolymerizable compound that is soluble in the monomer are known as *macroporous* or *macroreticular resins* (see Section 3.1). Other naturally porous resins are known as *gel resins*.

**Polyacrylic Anion Exchangers.** Between 1970 and 1972, a new type of anion-exchange resin with a polyacrylic matrix appeared on the market. This possesses exceptional resistance to organic fouling and a very high mechanical stability due to the elasticity of the polymer.

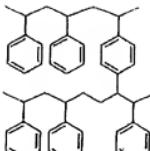
**Uniform Size Resins.** In the 1980s and 1990s, several producers developed new manufacturing technologies aimed at producing resins with particles of almost identical size.

## 2. Structures of Ion-Exchange Resins

An ion exchanger consists of the polymer matrix and the functional groups that interact with the ions. This article deals only with organic ion exchangers; inorganic ion exchangers are of minor importance and are primarily layer silicates and zeolites (→ Silicates, → Zeolites).

### 2.1. Polymer Matrices

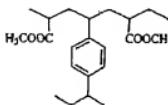
**Polystyrene Matrix.** (→ Polystyrene and Styrene Copolymers). The polymerization of styrene [100-42-5] (vinylbenzene) under the influence of a catalyst (usually an organic peroxide) yields linear polystyrene [9003-53-6]. Linear polystyrene is a clear moldable plastic which is soluble in certain solvents (e.g., styrene or toluene) and has a well-defined softening point. If a proportion of divinylbenzene is mixed with styrene, the resultant polymer becomes cross-linked and is then completely insoluble.



Cross-linked polystyrene

In the manufacture of ion-exchange resins, polymerization generally occurs in suspension. Monomer droplets are formed in water and, upon completion of the polymerization process, become hard spherical beads of the polymer.

**Polyacrylic Matrix.** Matrices for ion exchangers can also be obtained by polymerizing an acrylate, a methacrylate, or an acrylonitrile, any of which can be cross-linked with divinylbenzene [105-06-6] (DVB) (→ Polyacrylamides and Poly(Acrylic Acids)); → Polyacrylates.



Cross-linked polymethacrylate

**Other Types of Matrix.** Other types of matrix include

- 1) **Phenol-formaldehyde** resins (→ Phenolic Resins) which show interesting adsorption properties
- 2) **Polyalkylamine resins**, obtained from polyamines by condensation with epichlorohydrin, which gives an anion exchanger directly in a single step.

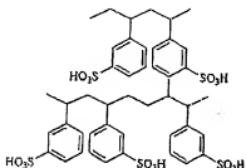
## 2.2. Functional Groups

### 2.2.1. Cation-Exchange Resins

Cation-exchange resins in current use can be separated into two classes according to their active groups:

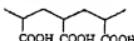
- 1) Strongly acidic (sulfonic groups)
- 2) Weakly acidic (carboxylic groups)

**Strongly Acidic Cation-Exchange Resins.** Chemically inert polystyrene beads are treated with concentrated sulfuric or chlorosulfonic acid to give cross-linked polystyrene 3-sulfonic acid. This material is the most widely used cation-exchange resin and is strongly acidic.



**Examples:** Amberlite IR 120, Dowex HCR, Lewatit S100.

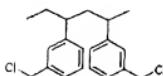
**Weakly Acidic Carboxylic Cation-Exchange Resins.** The weakly acidic resins are almost always obtained by hydrolysis of polymethylacrylate or polyacrylonitrile to give a poly(acrylic acid) matrix.



**Examples:** Amberlite IRC 86, Lewatit CNP.

### 2.2.2. Anion-Exchange Resins

**Polystyrene Materials.** Cross-linked polystyrene beads are treated with chloromethyl methyl ether under anhydrous conditions, with either aluminum chloride or tin(IV) chloride as catalyst. Chloromethylated polystyrene is obtained:



In a second stage, the chlorine in the chloromethylated group can be replaced by an amine

or even by ammonia. Depending on the reaction selected, the anion exchanger obtained may be strongly to weakly basic. The degree of basicity can be "made to measure" because of the large number of amines available. The anion exchangers listed below are arranged in order of decreasing basicity:



where R can be

$\text{--CH}_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$	e.g., Amberlite IRA402
$\sim\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{OHC}^-$	e.g., Amberlite IRA410
$\sim\text{CH}_2\text{N}(\text{CH}_3)_3$	e.g., Amberlite IRA96

Resins with quaternary ammonium groups are strongly basic. Those with benzyltrimethylammonium groups are known as type 1 and are the most strongly basic, whereas those with benzylidimethylethanolammonium groups are known as type 2 and are slightly less basic.

Type 1 resins are used when total removal of anions, even those of weak acids (including silica), is essential. Type 2 resins are also basic enough to remove all anions, but they release the anions more easily during regeneration with caustic soda; as a result, they have a high exchange capacity and a better regeneration efficiency (see Section 7.1). Unfortunately, they are chemically less stable and produce greater silica leakage than type 1 resins.

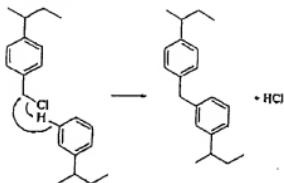
Resins whose active group is an amine are generally denoted as weakly basic, although their basicity may vary considerably. Tertiary amines are sometimes called medium-base or intermediate-base resins, whereas primary amines are very weakly basic and are rarely used.

The most widely used weakly basic resins contain tertiary amino groups and adsorb any strong acids present in the solution to be treated but do not affect neutral salts or weak acids.

Manufacturers do not always indicate the chemical structure of their exchangers in their literature. Care should therefore be taken not to assume that resins are chemically identical

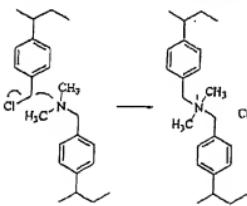
merely because they have similar general characteristics.

**Secondary and Tertiary Cross-Linking.** During chloromethylation, a side reaction may occur in which the chloromethyl group of a chloromethylated benzene ring reacts with an unconverted ring, to yield a methylene bridge. These bridges form additional cross-links in the polystyrene matrix:



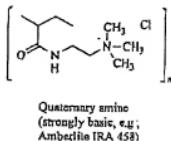
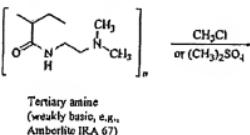
The amount of this secondary cross-linking can be adjusted by varying the conditions (quantity and type of catalyst, temperature) of the chloromethylation reaction. Most strongly basic and weakly basic polystyrene resins have some degree of secondary cross-linking.

Furthermore, during the amination of weakly basic resins, another type of cross-linking may be produced. This is called tertiary cross-linking and yields strongly basic quaternary groups in addition to the weakly basic tertiary groups.



**Polyacrylic Resins.** Polyacrylic resins are manufactured in a manner analogous to that used for polystyrene resins. Beads are prepared from an acrylic ester copolymerized with divinylbenzene by using suspension polymerization and free-radical catalysis. The polyacrylate formed is then given active groups by reaction with a

polyfunctional amine containing at least one primary amino group and one secondary or, more frequently, tertiary amino group. The primary amino group reacts with the polyester to form an amide, whereas the secondary or tertiary amino group forms the active group of the anion exchanger. This method always yields a weakly basic exchanger, which can be further treated with chloromethane or dimethyl sulfate to give a quaternary strongly basic resin:



In principle, a wide range of anion-exchange resins can be obtained by varying the type of ester chosen as the starting material and the polyamine used for activation. In practice, the range is limited by the availability and cost of raw materials.

### 2.2.3. Other Types of Ion-Exchange Resins

By using polymerization and activation methods analogous to those described above, a wide variety of functional groups can be grafted onto a given polymer. Some of these groups can be used for selective uptake of ions, principally metals (Table 1).

The thiol group forms very stable bonds with certain metals, particularly mercury. The iminodiacetic, aminophosphonic, and amidoxime groups form metal complexes whose stability depends mainly on the pH of the solution. Selective adsorption of certain metals can thus be achieved by varying the pH. These types of material are known as *chelating* or *complexing resins*.